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(54) **Process for the transformation of a vanadium/Phosphorous Mixed Oxide catalyst precursor into the active catalyst for the production of maleic anhydride**

(57) A Vanadium/Phosphorous Mixed Oxide catalyst precursor is transformed into the active catalyst for the production of maleic anhydride.

The activation takes place in a fluidized bed and includes the steps

- initial heating of the precursor
- further heating under superatmospheric pressure
- isothermal stage at superatmospheric pressure and finally
- cooling the activated catalyst obtained.

Catalysts activated according this procedure show high performance in the conversion of non aromatic hydrocarbons to maleic anhydride.

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## Description

The invention relates to a process for the transformation of a Vanadium/Phosphorus Mixed Oxide catalyst precursor into the active catalyst for the production of maleic anhydride and to a process for the production of maleic anhydride applying such an activated catalyst.

Maleic anhydride is a very important intermediate for manufacturing unsaturated polyester resins or a versatile intermediate for producing pharmaceuticals and agrochemicals.

Numerous catalysts based on a vanadium / phosphorus mixed oxide substantially in the form of vanadyl pyrophosphate are disclosed in the prior art as being useful for the conversion of different organic feed stock to maleic anhydride.

In general it is therefore known to prepare the active catalyst species through a multistep procedure which comprises:

- a) synthesis of a vanadyl hydrogen phosphate as precursor by contacting V-containing compounds, phosphorus containing compounds and optionally promoter component containing compounds under conditions sufficient to reduce the pentavalent vanadium to the tetravalent vanadium
- b) transformation of the vanadyl hydrogen phosphate precursor into the active catalyst substantially containing vanadyl pyrophosphate by calcination and finally
- c) ageing the active catalyst under reaction conditions.

One of the most critical steps in the catalyst preparation is the calcination procedure i.e. the transformation of the vanadyl hydrogen phosphate precursor into the active catalyst substantially containing vanadyl pyrophosphate.

US patent 5 137 860 discloses a process for the transformation of a vanadium / phosphorus mixed oxide oxidation catalyst precursor into the active catalyst for the partial oxidation of non aromatic hydrocarbons to maleic anhydride. The calcination of the precursor material is performed by a three-stage heat treatment comprising a) an initial heat up stage and an atmosphere selected from air, steam, inert gas and mixtures thereof, b) a rapid heat up stage at a programmed heat-up rate in a molecular oxygen / steam containing atmosphere and c) a maintenance finishing stage, first in a molecular oxygen / steam containing atmosphere and thereafter in a nonoxidizing steam containing atmosphere. According to this disclosure the calcination takes place in a fixed bed at atmospheric pressure conditions. As the splitting off of water during the calcination is endothermic it was found that remarkable temperature gradients in the fixed bed occur. This inhomogeneity in the temperature profile finally lead to a lower performance and a decreased attrition resistance of the catalytic system.

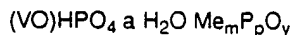
Object of the present invention therefore is to avoid this disadvantages of the state of the art catalytic system and to provide an improved process for the transformation of a Vanadium/Phosphorus Mixed Oxide catalyst precursor into the active catalyst for the production of maleic anhydride.

Another object of this invention is to provide a catalyst with optimal performance in the conversion of a non aromatic hydrocarbon to maleic anhydride.

Still another object of the invention is to provide an improved process for the preparation of maleic anhydride.

The objectives and advantages of the invention were achieved with the new process for the transformation of a Vanadium/Phosphorus Mixed Oxide catalyst precursor into the active catalyst according to claim 1, with the catalyst obtainable by the inventive transformation process according to claim 12 and with the process for the preparation of maleic anhydride applying the catalyst transformed according to the instant invention according to claim 13.

The inventive process comprises the transformation of a catalyst precursor represented by the formula



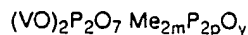
wherein Me is at least one promoter element selected from the group consisting elements from Group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIA, VIB AND VIIIA of the Periodic table of elements or mixtures thereof,

a is a number of from about 0,3 to about 0,7,

m is a number of from about 0 to about 0,3,

p is a number of from about 0 to about 0,3 and

y corresponds to the amount of oxygen necessary to satisfy the valence requirements of all elements present into an active catalyst represented by the formula



wherein m, p and y are as defined above which process comprises conducting in a fluidized bed the steps:

- a) an initial heating of the precursor to a temperature not to exceed about 250°C
- b) a further heating under super atmospheric pressure from about 200°C to a temperature of from at least

380°C to 600°C,

- c) maintaining the temperature reached at stage b) under super atmospheric pressure and
- d) cooling the activated catalyst.

5 The term "Periodic table of elements" as employed herein, refers to the Periodic table of elements published in Römpp Chemie Lexikon 9.ed, Georg Thieme Verlag, Stuttgart, volume 4, page 3285.

Me has the preferable meaning of lithium, zirconium, titanium, iron or niobium or of mixtures of these elements, a preferably is a number of about 0,5

10 m preferably is a number of from about 0 to about 0,1 and  
p preferably is a number of from about 0,1 to 0,2.

The phosphorus to vanadium- or P/V-atomic ratio therefore is expediently in the range of from about 1 to 1,3, preferably of from about 1,1 to about 1,2.

15 Catalyst precursor materials suitable for the use in the process of the instant invention are those known in the art e.g. from US patent 4 594 433, US patent 5 137 860 or US patent 4 668 652.

The preparation of the precursors accordingly is including reaction of the vanadium component, the phosphorus component and optionally the promoter component in either aqueous or organic medium. Organic reaction media such as for instance a primary and a secondary alcohol or mixtures thereof are usually preferred. Most preferred is isobutyl  
20 alcohol or benzyl alcohol or mixtures thereof. Depending on the preparation conditions the alcohol may remain trapped or intercalated to a remarkable content in the precursor structure.

Although well known in the art the vanadium component of the precursor may be obtained from a trivalent, tetravalent or a pentavalent vanadium compound. Representative examples, although not limiting, are vanadium trichloride, vanadium tetrachloride, vanadium dioxide, vanadium pentoxide or vanadium oxytribromide. Vanadium pentoxide is the preferred compound.

25 Examples of the phosphorus compound, although not limiting, are phosphorus acid or phosphoric acid.

Depending of the valence of the vanadium compound the reaction can either be conducted under non-oxidising conditions or under reducing conditions in order to reduce a pentavalent vanadium compound to the tetravalent form.

The catalyst precursor once prepared, recovered and dried is in view of its activation treatment in the fluidized bed according to the invention preferably formed into defined structures with defined properties as to attrition resistance or mechanical properties. Such procedures in general include a wet grinding process of the dried precursor to a particle  
30 size of less than 10  $\mu\text{m}$ , preferably less than 3  $\mu\text{m}$ . Additives may be added at this stage to improve resistance to attrition following the disclosure of e.g. US patent 4 511 670.

Following this previous art a recovery step e.g. by spray drying, calcining, additional grinding in presence of a controlled amount of an acid, typically of phosphoric acid and a finally recovering and forming of the precursor material by e.g. spray drying may follow.

35 Preferably the precursor is collected in a spherical shape, which form is most suitable for its use in a fluidized bed reactor.

The transformation of the precursor material as defined by general formula I into the active catalyst in general comprises four steps, which are conducting in a fluidized bed the steps:

- a) an initial heating of the precursor to a temperature not to exceed about 250°C
- b) a further heating under super atmospheric pressure from about 200°C to a temperature of from at least 380°C to 600°C,
- 45 c) maintaining the temperature reached at stage b) under super atmospheric pressure and
- d) cooling the activated catalyst.

According to the invention the transformation into the active catalyst takes place in a fluidized bed which expediently means under conditions which allow optimal fluidization of the catalyst bed. Such conditions are preferably expressed with the superficial velocity which is defined as the volume of gaseous feed at the current temperature and pressure conditions per second expressed in  $\text{m}^3\text{s}^{-1}$  divided by the surface area of the catalyst bed expressed in  $\text{m}^2$  leading to the superficial velocity expressed in  $\text{ms}^{-1}$ .

The superficial velocity is usually adjusted to a range of from about 0,01  $\text{ms}^{-1}$  to 0,5  $\text{ms}^{-1}$ , preferably from about 0,02  $\text{ms}^{-1}$  to 0,2  $\text{ms}^{-1}$ , as a rule during the whole phase of transformation of the precursor into the active catalyst.

55 Within the initial heat up stage a) the precursor is heated in a conventional atmosphere e.g. like air, steam, inert gas or mixtures thereof, under atmospheric pressure or super atmospheric pressure and at any convenient heat up rate to a temperature not to exceed about 250°C.

Superatmospheric pressure in the following is expressed as absolute pressure.

In a preferred embodiment the precursor is heated in air under super atmospheric pressure of at least 1,1 bar, more

preferable 2 bar to 3 bar, at a heat up rate of about 1°C / minute to 5°C / minute to a temperature not to exceed about 200°C.

Within the activation stages b) and c) super atmospheric pressure is a mandatory parameter which surprisingly has the effect to further improve the performance of the catalytic system. Expediently super atmospheric pressure in these stages of at least 1,1 bar, preferably of from about 2 to about 3 bar is applied.

Stage b) comprises a further heat up stage where the temperature reached in stage b is further increased of from about 200°C to a temperature of at least 380°C to not to exceed about 600°C, preferably from about 200°C to about 400°C to 450°C, at a controlled heat up rate, in a defined atmosphere and under the fluidized bed and pressure conditions as described herein before.

Expediently a heat up rate of from about 0,1 °C / minute to about 10°C / minute, preferably of from about 1°C / minute to about 4°C / minute is selected.

The atmosphere necessary for stage b) is a composition of oxygen or an oxygen containing gas, of an inert gas and of steam, expediently containing 1 to 20 % by volume, preferably 2 to 10 % by volume of oxygen, 10 to 80 % by volume, preferably 30 to 70 % by volume of steam (calculated as H<sub>2</sub>O) and the balance inert gas.

The source of oxygen can either be air or molecular oxygen, preferably air. As inert gas nitrogen or a noble gas like helium or argon may be applied.

Within the isothermal stage c) the temperature reached in stage b) is maintained over at least 0,5 hours, preferably for a period of 1 to 5 hours in a controlled atmosphere and under the fluidized bed and pressure conditions as described herein before.

The atmosphere necessary for stage c) is a composition of steam and of an inert gas and if necessary of oxygen or an oxygen containing gas, expediently containing 10 to 80 % by volume, preferably 30 to 70 % by volume of steam (calculated as H<sub>2</sub>O) and 0 to 20 % by volume, preferably 2 to 10 % by volume of oxygen and the balance inert gas.

The source of oxygen can either be air or molecular oxygen, preferably air. As inert gas nitrogen or a noble gas like helium or argon may be applied.

Within the cooling stage d) the now activated catalyst is brought to ambient temperature.

Although the conditions are not critical it is preferred to perform this stage in an inert atmosphere and under the fluidized bed and pressure conditions as described herein before.

The cooling rate preferably should not exceed 5°C / minute.

After this transformation performed according to the invention the catalyst is ready to be applied for the conversion of non aromatic hydrocarbons to maleic anhydride. Surprisingly and this is a further important aspect of the invention the catalyst needs no further ageing under process conditions. The catalyst exhibits immediate activity and selectivity right from the beginning of the conversion providing excellent yields of maleic anhydride.

The process for the conversion of non aromatic hydrocarbons to maleic anhydride is well known in the art e.g. from US patent 4 594 433, US patent 5 137 860 or US patent 4 668 652.

In general the non aromatic hydrocarbon is converted with oxygen or an oxygen containing gas at a temperature from about 320°C to 500°C to maleic anhydride. The non aromatic hydrocarbon is expediently selected from a saturated or unsaturated C<sub>4</sub> to C<sub>10</sub> hydrocarbon or mixtures thereof. Most preferred hydrocarbon is n-butane. The feed gas is as a rule composed of a mixture of the hydrocarbon and of the oxygen or oxygen containing gas, preferably air having a ratio oxygen to hydrocarbon as a rule of from 15:1 to 1:1.

The conversion can take place in a fixed bed or fluidized bed reactor, but in particular is performed in a fluidized bed reactor.

The following examples are given by way of illustration only and are not construed as limiting since various modifications within the spirit of the invention are apparent to those skilled in the art from this description.

## Examples

### Example 1 (comparison)

Into a three-necked flask, capacity 5 litres, fitted with thermometer, mechanical stirrer, glass distillation packed column with reflux condenser and Dean-Stark water separator, are introduced 2 litres of isobutanol and 404 g of H<sub>3</sub>PO<sub>4</sub> (100%). The mixture is brought to reflux and then a suspension of 326 g of V<sub>2</sub>O<sub>5</sub> in 1000 ml of isobutanol is slowly added (in about 1 hour).

During addition of the V<sub>2</sub>O<sub>5</sub>, a quantity of isobutanol equal to that added with V<sub>2</sub>O<sub>5</sub> is distilled thus removing from the reaction mixture the water that forms during the reaction.

At the end of the addition of V<sub>2</sub>O<sub>5</sub> the reflux is continued for another two hours, thus separating further reaction water. The slurry is cooled and the blue solid is filtered and dried at 140°C. In this manner the V-P-O complex oxide precursor of the catalyst is obtained. The catalyst precursor once prepared is formed into a structure with defined properties of attrition resistance by spray drying as described in U.S. Patent 4,654,425 (example 1).

The material recovered from spray drying was loaded in stainless steel baskets, and put in a forced-ventilation oven. An

atmosphere of  $N_2$  was maintained in the oven during the calcination and the precursor was heated at a programmed heating rate of about  $9^\circ\text{C}/\text{min}$  from room temperature to  $550^\circ\text{C}$ . At  $550^\circ\text{C}$ , the catalyst was kept under isothermal conditions for 5h, followed by cooling down to room temperature. This procedure is referred to as the standard procedure of calcination.

#### Example 2 (comparison)

This example illustrates the transformation of a vanadium phosphorus oxide precursor prepared according to Example 1 into an active catalyst in accordance with the procedure described in Example 3 Part D of US Patent 5,137,860.

The material recovered from spray drying was loaded into a stainless steel tray and placed in a box oven. The precursor was heated with the hydrothermal treatment according to the following procedure:

- a) from  $25^\circ\text{C}$  to  $275^\circ\text{C}$  in air with no control of the heat-up stage;
- b) from  $180^\circ\text{C}$  to  $425^\circ\text{C}$  in a mixture of air (75mol%) and steam (25%mol) at a programmed rate of  $4^\circ\text{C}/\text{min}$ ;
- c) isothermal step at  $425^\circ\text{C}$  with the same mixture as above for 1 h;
- d) isothermal step at  $425^\circ\text{C}$  in nitrogen (50%mol) and steam (50%mol), for 6 h;

#### Example 3 (comparison)

The procedure hereinafter described is referred to as the hydrothermal method of calcination in a fluid bed at atmospheric pressure. The procedure consists of a thermal treatment in the presence of steam. The treatment was carried out at temperatures not higher than  $450^\circ\text{C}$ . The material recovered from spray drying was loaded in stainless steel fluid bed reactor and treated at atmospheric pressure with the hydrothermal treatment according to the following procedure:

- a) from  $25^\circ\text{C}$  to  $180^\circ\text{C}$  in air in 40';
- b) from  $180^\circ\text{C}$  to  $425^\circ\text{C}$  in a mixture of air (27vol%) and steam (73%vol) at a programmed rate of  $1.5^\circ\text{C}/\text{min}$ ;
- c) isothermal step at  $425^\circ\text{C}$  with the same mixture as above for 2 h;
- d) isothermal step at  $425^\circ\text{C}$  in nitrogen (27%vol) and steam (73%vol), for 3 h;
- e) cooling in a mixture of nitrogen and steam.

#### Example 4 (invention)

The procedure hereinafter described is referred to as the hydrothermal method of calcination in a fluid bed under pressure. The procedure consists of a thermal treatment in the presence of steam. The treatment was carried out at temperatures not higher than  $450^\circ\text{C}$ . The material recovered from spray drying was loaded in stainless steel fluid bed reactor and treated with the hydrothermal treatment under pressure (3 bar) and maintaining a superficial velocity of  $0.03\text{ ms}^{-1}$  according to the following procedure:

- a) from  $25^\circ\text{C}$  to  $180^\circ\text{C}$  in air, at a programmed rate of  $4^\circ\text{C}/\text{min}$ ;
- b) from  $180^\circ\text{C}$  to  $425^\circ\text{C}$  in a mixture of air (70%vol) and steam (30%vol); at a programmed rate of  $1.5^\circ\text{C}/\text{min}$ ;
- c) isothermal step at  $425^\circ\text{C}$  with the same mixture as above for 2 h;
- d) isothermal step at  $425^\circ\text{C}$  in nitrogen (70% vol) and steam (30%vol) for 3 h;
- e) cooling in a mixture of nitrogen and steam at a programmed rate of  $2^\circ\text{C}/\text{min}$ .

#### Example 5 (invention)

The precursor was treated as in example 4, except that the superficial velocity was  $0.05\text{ ms}^{-1}$ .

#### Example 6 (invention)

The precursor was treated as in example 4, except for the step d) which was carried out in a mixture of nitrogen and steam for 6 h.

#### Example 7 (invention)

The precursor was treated as in example 4, except that the count of oxygen in feed was 4%vol. The activity test was performed as in Example 1 and the catalytic behaviour is given in Table 1.

**Testing of the activated catalysts in the conversion of n-butane to maleic anhydride:**

The catalytic tests were done in a fluid bed pilot-plant, glass, plug-flow reactor at atmospheric pressure, which was loaded with 500 ml of catalyst. The products were collected and absorbed in water and analysed by means of gas chromatography. The performance of the catalysts was determined on the basis of the weight of butane fed to the reactor, amount of maleic anhydride (MA) recovered in the wash-water (acidimetry) and the amount of butane in the off gases during a specified period of time.

In order to provide a basis for comparison, the following conditions were maintained during the activity tests:

- Reaction temperature: 360-440°C.
- n-Butane conc. in feed: 4 vol%.
- Air flow rate: 75 Nl/h.
- Superficial velocity: 0.03 ms<sup>-1</sup>.

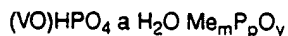
- The reaction conditions and the results are recorded in the following Table which reports the temperature at which 81% n-butane conversion is achieved, and the yield and selectivity to maleic anhydride at this conversion.

Table

catalyst according to example:	Temperature	MA yield	MA selectivity
1 (comparison)	425	52.3	64.6
2 (comparison)	430	53.4	65.9
3 (comparison)	415	55.1	68.0
4	420	57.5	71.0
5	425	57.9	70.5
6	420	56.9	70.2
7	425	58.1	71.7

**Claims**

1. Process for the transformation of a catalyst precursor represented by the formula



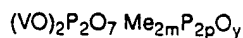
wherein Me is at least one promoter element selected from the group consisting elements from Group IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIA, VIB and VIIIA of the Periodic table of elements or mixtures thereof,

a is a number of from about 0.3 to about 0.7,

m is a number of from about 0 to about 0.3

p is a number of from about 0 to about 0.3 and

y corresponds to the amount of oxygen necessary to satisfy the valence requirements of all elements present into an active catalyst represented by the formula

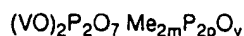


wherein m, p and y are as defined above, which process comprises conducting in a fluidized bed the steps:

- a) initial heating of the precursor to a temperature not to exceed about 250°C
- b) further heating under superatmospheric pressure from about 200°C to a temperature of from at least 380°C to 600°C,

c) maintaining the temperature reached at stage b) under superatmospheric pressure and  
d) cooling the activated catalyst.

2. The process according to claim 1 characterised in that superatmospheric pressure is maintained over all steps a), b), c) and d).
3. The process according to at least one of the claims 1 to 2 characterised in that superatmospheric pressure or at least 1,1 bar is applied.
4. The process according to at least one of the claims 1 to 3 characterised in that superatmospheric pressure of from about 2 bar to about 3 bar is applied.
5. The process according to at least one of the claims 1 to 4 characterised in that the fluidized bed is run with a superficial velocity adjusted in the range of from about  $0.01 \text{ ms}^{-1}$  to  $0.5 \text{ ms}^{-1}$ .
6. The process according to at least one of the claims 1 to 5 characterised in that step a) comprises initial heating of the precursor to a temperature not to exceed  $200^\circ\text{C}$ .
7. The process according to claim 6 characterised in that step a) comprises initial heating of the precursor in an atmosphere of air.
8. The process according to at least one of the claims 1 to 7 characterised in that step b) comprises further heating from about  $200^\circ\text{C}$  to about  $400^\circ\text{C}$  to  $450^\circ\text{C}$  applying a heat-up rate of from about  $0.1^\circ\text{C/minute}$  to  $10^\circ\text{C/minute}$ .
9. The process according to at least one of the claims 1 to 8 characterised in that step b) comprises further heating in an atmosphere composed of 1 to 20% by volume of oxygen or of an oxygen containing gas, of 10 to 80% by volume of steam and of the balance inert gas.
10. The process according to at least one of the claims 1 to 9 characterised in that step c) comprises maintaining the temperature reached in step b) in an atmosphere composed of 0 to 20% by volume of oxygen or of an oxygen containing gas, of 10 to 80% by volume of steam and of the balance inert gas.
11. The process according to at least one of the claims 1 to 10 characterised in that step d) comprises cooling the activated catalyst in an inert atmosphere at a rate not to exceed  $5^\circ\text{C/minute}$ .
12. Active catalyst represented by the formula



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- wherein m, p and y are as defined above obtainable by the process of at least one of the claims 1 to 11.
13. Process for the production of maleic anhydride which comprises converting a feeding gas composed of a non aromatic hydrocarbon and of oxygen or of an oxygen containing gas in the presence of an active catalyst obtainable by the process of at least one of the claims 1 to 11 at a temperature of from about  $320^\circ\text{C}$  to about  $500^\circ\text{C}$ .



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# EUROPEAN SEARCH REPORT

Application Number  
EP 97 10 6932

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D, Y	US 5 137 860 A (J.R.EBNER) * the whole document *	1-13	B01J27/198 C07C51/215 C07C57/145
Y	US 3 915 892 A (J.P.HARRISON) * column 10, line 40 - column 11, line 16; example 3 *	1-13	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01J C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 August 1997	Examiner Rotsaert, L
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

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